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Restoration of Universality for the Rod-to-Coil Transition Scaling in the Infinite-Dimensionality Limit: Exact Results for Directed Walks

V. Privman[1] **and N. M. Švrakić**[1]

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We derive scaling forms for the thermodynamic and correlation quantities for the turn-weighted fully and partially directed self-avoiding walks on the hypercubic lattices in $d \geqslant 2$. In the grand canonical (fixed fugacity per step) ensemble, the conformational rod-to-coil transition sets up in the regime $w\bar{N} = O(1)$, where w is the weight of each 90° turn and $\bar{N}$ is the (fugacity-dependent) average number of steps. Contrary to the conventional critical phenomena wisdom, the scaling functions for the two different walk models, directed and partially directed, become universal only in the limit $d \to \infty$.

KEY WORDS: Polymer scaling; universality; critical point; random walks.

1. INTRODUCTION

Recent studies of the conformational rof-to-coil transition of a single linear polymer chain have concentrated on the scaling in the lattice models. Both self-avoiding walks (SAW) and Gaussian walks have been investigated: see Refs. 1–4 and earlier literature cited therein. Unusual aspects of the rod-to-coil transition scaling include nonuniversality of the scaling functions for several SAW and Gaussian models, and suppression of the self-avoidance effects in the large-persistence-length regime. Approximate Flory-type argument[(5)] suggests a crossover to Gaussian scaling for SAW models in $d > 2$. This property should become exact in the $d \to \infty$ limit.

In $d = 2$, the nonuniversality of the scaling functions has been demonstrated explicitly for *directed* walk models.[(4)] In this work, we report

[1] Department of Physics, Clarkson University, Potsdam, New York 13676.

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results for the fully directed (FD) and partially directed (PD) SAWs on the hypercubic lattices in $d \geqslant 2$. We find that the scaling functions become universal only in the $d \to \infty$ limit.

The directed SAW models have no really long-range self-avoidance effects. Indeed, for the FD walks considered in Section 2, the self-avoidance condition is irrelevant. For the PD walks, which are discussed in Section 3, the self-avoidance constraint reduces to the "no immediate returns" condition. However, the directed walk models are exactly solvable (see Refs. 4 and 6–8 and literature cited therein), and exhibit scaling behaviors different from the isotropic walks. It is therefore instructive to study the rod-to-coil transition scaling properties for directed models in detail. Some general observations on the nature of the scaling functions, summarized in Section 4, should be applicable for the more realistic isotropic lattice walk models.

2. FULLY DIRECTED WALKS ON THE HYPERCUBIC LATTICES

A FD walk on the hypercubic lattice in d dimensions consists of a sequence of N steps $+a\hat{x}_i$ $(i = 1, 2,..., d)$, where a is the lattice spacing, and $\hat{x}_i$ denote unit vectors along the lattice axes $X_1,..., X_d$. For each N-step walk ($N = 1, 2,...$), we denote by n_i the number of the corresponding $+a\hat{x}_i$ steps:

$$N = \sum_{i=1}^{d} n_i \tag{2.1}$$

Let T denote the number of 90° turns in a walk, and assign weights $x_i^{n_i}$ per $+a\hat{x}_i$ steps. Then the generating function can be defined via

$$G(x_j; w) = \sum_{\text{all walks}} \left(w^T \prod_{i=1}^{d} x_i^{n_i} \right) \tag{2.2}$$

The sum in (2.2) is over all possible walks starting at a fixed origin. We can also define partial generating function G_i for all walks with their *first step* along the X_i axis,

$$G(x_1,..., x_d; w) = \sum_{i=1}^{d} G_i(x_1,..., x_d; w) \tag{2.3}$$

By extending the method of Ref. 4, we can calculate the generating function G by first deriving recursion relations among the G_i. These are

$$G_i = x_i + x_i G_i + w x_i \sum_{\substack{j=1 \\ j \neq i}}^{d} G_j \tag{2.4}$$

Equation (2.4) expresses the fact that a walk starting with the $+a\hat{x}_i$ step can terminate (weight x_i), continue straight (weight $x_i G_i$), or turn (weights $w x_i G_j$). It is equivalent to

$$G_i = \frac{x_i}{1-(1-w)\,x_i}\,(1+wG) \tag{2.5}$$

and, when summed over i, gives an equation for G. Thus, we obtain

$$G(x_j; w) = \frac{S_d}{1-wS_d} \tag{2.6}$$

where

$$S_d \equiv \sum_{i=1}^{d} \frac{x_i}{1-(1-w)\,x_i} \tag{2.7}$$

The grand canonical partition function, in the ensemble with the fugacity weight z^N assigned for each N-step walk, is given by

$$Z(z; w) = G(z,..., z; w) = \frac{dz}{1-[1+(d-1)w]z} \tag{2.8}$$

The average number of steps in a walk is given by

$$N(z; w) = z\,\frac{\partial \ln Z}{\partial z} = \frac{1}{1-z[1+(d-1)w]} \tag{2.9}$$

In the $w \to 0$ limit, we have

$$N(z; 0) = (1-z)^{-1} \equiv \bar{N}(z) \tag{2.10}$$

As discussed in Ref. 4, the scaling limit corresponds to $w \to 0$, $\bar{N} \to \infty$, with the scaling combination

$$\tau = w\bar{N} = w/(1-z) \tag{2.11}$$

taking values of $O(1)$. For fixed "stiffness" w, very large chains will be coiled provided $N \gg w^{-1}$. For fixed length N, very stiff chains ($w \ll N^{-1}$) will be rodlike. The transition occurs when w and N^{-1} are comparable, i.e., τ is of order 1. The use of $\bar{N}$ is for technical convenience only.[4] In principle, the scaling relations could be formulated in terms of $N(z; w)$. The scaling relations take the form

$$\frac{Z(z; w)}{Z(z; 0)} \equiv \frac{1}{1-(d-1)\,w(\bar{N}-1)} \approx \frac{1}{1-(d-1)\tau} = A(c\tau) \tag{2.12}$$

$$\frac{N(z; w)}{N(z; 0)} \approx \frac{1}{1-(d-1)\tau} = B(c\tau) \tag{2.13}$$

Here the scaling functions A and B are defined in terms of the scaling field

$$g \equiv c\tau \tag{2.14}$$

where the metric factor c can be determined[4] from the fixed-w critical point value $z_c(w)$. Indeed, for fixed $w > 0$, the functions $Z(z; w)$ and $N(z; w)$ diverge as

$$z \to z_c(w) \equiv [1 + (d-1)w]^{-1} \tag{2.15}$$

The constant c is given by the scaling limiting behavior of the combination

$$[1 - z_c(w)]\ \bar{N}(z) \approx c\tau \tag{2.16}$$

Thus, we obtain

$$c_{\text{FD}} = d - 1 \tag{2.17}$$

and

$$A_{\text{FD}}(g) = B_{\text{FD}}(g) = (1 - g)^{-1} \tag{2.18}$$

We now turn to the calculation of correlation lengths. The unit vector along the directed or "time" axis is

$$\hat{e}_{\|} = \frac{1}{\sqrt{d}} \sum_{i=1}^{d} \hat{x}_i \tag{2.19}$$

The parallel displacement after N steps is therefore given by

$$r_{\|} = \mathbf{r} \cdot \hat{e}_{\|} = \left(\sum_{i=1}^{d} a n_i \hat{x}_i \right) \cdot \hat{e}_{\|} = \frac{a}{\sqrt{d}} N \tag{2.20}$$

where $\mathbf{r}$ is the origin-to-end vector. It follows from (2.20) that the first-moment parallel correlation length[4] is simply

$$\xi_{\|}^{(1)}(z; w) \equiv \frac{a}{\sqrt{d}} N(z; w) \tag{2.21}$$

We also consider the second-moment parallel correlation length defined by

$$[\xi_{\|}^{(2)}(z; w)]^2 = \left(\sum_{\text{all walks}} r_{\|}^2 z^N w^T \right) \Big/ Z(z; w) \tag{2.22}$$

We have

$$[\xi_{\parallel}^{(2)}(z; w)]^2 = \frac{a^2}{d} Z^{-1} \left(z \frac{\partial}{\partial z}\right)^2 Z$$
$$= \frac{a^2}{d} \frac{1 + [1 + (d-1)w]z}{\{1 - [1 + (d-1)w]z\}^2} \tag{2.23}$$

The first-moment perpendicular correlation length vanishes by symmetry. The second-moment definition is analogous to (2.22), but with

$$r_{\perp}^2 = r^2 - r_{\parallel}^2 = a^2 \sum_{i=1}^{d} n_i^2 - r_{\parallel}^2 \tag{2.24}$$

Thus,

$$[\xi_{\parallel}^{(2)}]^2 + [\xi_{\perp}^{(2)}]^2 = a^2 Z^{-1} \sum_{i=1}^{d} \left[\left(x_i \frac{\partial}{\partial x_i}\right)^2 G(x_1, ..., x_d; w)\right]_{x_i = z}$$
$$= a^2 d Z^{-1} \left[\left(x \frac{\partial}{\partial x}\right)^2 G(x, z, ..., z; w)\right]_{x=z} \tag{2.25}$$

The resulting expression for $\xi_{\perp}^{(2)}$ is

$$[\xi_{\perp}^{(2)}(z; w)]^2 = \frac{a^2}{d} \frac{(d-1)[1 + (1-w)z]}{[1 - (1-w)z]\{1 - z[1 + (d-1)w]\}} \tag{2.26}$$

The scaling relations for the correlation lengths take the forms

$$\frac{\xi_{\parallel}^{(k)}(z; w)}{\xi_{\parallel}^{(k)}(z; 0)} \approx P^{(k)}(c\tau), \qquad k \geq 1 \tag{2.27}$$

$$\frac{\xi_{\perp}^{(k)}(z; w)}{\xi_{\perp}^{(k)}(z; 0)} \approx Q^{(k)}(c\tau), \qquad k \text{ even} \tag{2.28}$$

Explicit calculation yields

$$P_{\text{FD}}^{(1)}(c\tau) = P_{\text{FD}}^{(2)}(c\tau) = \frac{1}{1 - (d-1)\tau} \tag{2.29}$$

$$Q_{\text{FD}}^{(2)}(c\tau) = \frac{1}{\{(1+\tau)[1 - (d-1)\tau]\}^{1/2}} \tag{2.30}$$

Note that for fixed $w > 0$ the results (2.8), (2.21) with (2.9), (2.23), and (2.26) verify the exponent values $\gamma = 1$, $\nu_{\perp} = 1/2$, and $\nu_{\parallel} = 1$ for all $d \geq 2$. These values were predicted by Cardy[7] from field-theoretical considerations.

3. PARTIALLY DIRECTED SELF-AVOIDING WALK MODEL

A partially directed (PD) SAW consists of $+a\hat{x}_i$ $(i=1,..., d-1)$ and $\pm a\hat{x}_d$ steps. Thus, we single out the X_d axis as a "two-way" direction. The unit vector along the directed or "time" axis is given by

$$\hat{e}_{\parallel}=\frac{1}{(d-1)^{1/2}}\sum_{i=1}^{d-1}\hat{x}_i \tag{3.1}$$

As long as only one axis is undirected, the problem is exactly solvable. The unbiased, $w=1$ model in $d=2$ has attracted much attention: consult Refs. 4 and 6–8 for the literature. (In fact, the PD model had been much more "popular" than the FD model!) The solvability of the $d>2$ PD SAW model was noted by Szpilka,[8] who reported that $\gamma=1$ for all $d\geqslant 2$. Redner and Majid[6] derived a variant of the generating function [their Eq. (7)] which is consistent with our results (see below).

Let n_i $(i=1,..., d-1)$ and $n_{\pm}$ denote the number of the $+a\hat{x}_1,...,$ $+a\hat{x}_{d-1}$, $\pm a\hat{x}_d$ steps in a given N-step walk, where

$$N=\sum_{i=1}^{d-1} n_i+n_+ +n_- \tag{3.2}$$

We introduce the generating function

$$G(x_1,..., x_{d-1}; x_+, x_-; w)=\sum_{\text{all walks}}\left(w^T x_+^{n_+} x_-^{n_-}\prod_{i=1}^{d-1} x_i^{n_i}\right) \tag{3.3}$$

where the notation for the step weights is self-explanatory. The partial generating functions for walks with the first steps $+a\hat{x}_1,..., +a\hat{x}_{d-1}$, $\pm a\hat{x}_d$ will be denoted $G_1,..., G_{d-1}$, $G_{\pm}$, respectively. We will also use the function

$$F=G-G_+ -G_- =\sum_{i=1}^{d-1} G_i \tag{3.4}$$

The recursion relations for G_i $(i<d)$ are similar to those for the FD model (Section 2); we have

$$G_i=x_i+x_iG_i+wx_i\left(\sum_{\substack{j=1\\ j\neq i}}^{d-1} G_j+G_+ +G_-\right) \tag{3.5}$$

This relation can be rearranged to yield

$$G_i=\frac{x_i}{1-(1-w)\,x_i}(1+wF+wG_+ +wG_-) \tag{3.6}$$

When summed over $i = 1, \ldots, d-1$, (3.6) reduces to

$$F = S_{d-1}(1 + wF + wG_+ + wG_-) \tag{3.7}$$

where S_d is defined in (2.7). The recursion relations for $G_\pm$ read

$$G_+ = x_+ + x_+ G_+ + w x_+ F \tag{3.8}$$

$$G_- = x_- + x_- G_- + w x_- F \tag{3.9}$$

The new feature here is the absence of the G_- term in the relation (3.8) for G_+, and of the G_+ term in (3.9): this is the only manifestation of self-avoidance for the PD SAW model. Equations (3.7)–(3.9) form a system of linear equations for F and $G_\pm$. Solving them, one obtains the total generating function as the sum of F, G_+, and G_-,

$$G(x_1, \ldots, x_{d-1}; x_+, x_-; w) = \frac{S_{d-1} + R + wRS_{d-1}}{1 - wS_{d-1} - w^2 RS_{d-1}} \tag{3.10}$$

where

$$R(x_\pm) = \frac{x_+}{1 - x_+} + \frac{x_-}{1 - x_-} \tag{3.11}$$

The partition function is obtained by putting all the x's to z in (3.10). Thus,

$$Z(z; w) = \frac{z[(d+1)(1-z) + 2dwz]}{1 - 2z - (d-2)\,wz - [2(d-1)\,w^2 - (d-2)w - 1]\,z^2} \tag{3.12}$$

and the scaling function, defined as in (2.12), is given by

$$A_{\text{PD}}(c\tau) = \frac{1 + d(1 + 2\tau)}{(d+1)[1 - (d-2)\tau - 2(d-1)\,\tau^2]} \tag{3.13}$$

In order to identify c_{PD}, we first calculate the location of the singularity of $Z(z; w)$,

$$z_c(w) = \frac{2}{2 + w[d - 2 + (d^2 + 4d - 4)^{1/2}]} \tag{3.14}$$

The metric factor c is then obtained by using (2.16),

$$c_{\text{PD}} = \frac{d - 2 + (d^2 + 4d - 4)^{1/2}}{2} \tag{3.15}$$

The expression for the average number of steps $N(z; w)$ is very long; we only report

$$N(z; 0) = (1 - z)^{-1} \equiv \bar{N}(z) \tag{3.16}$$

and the scaling form [defined as in (2.13)]

$$B_{\mathrm{PD}}(c\tau)=\frac{1+d(1+4\tau)+2(2d-1)\,\tau^2}{[1+d(1+2\tau)][1-(d-2)\tau-2(d-1)\,\tau^2]} \tag{3.17}$$

In order to calculate the correlation lengths, we first note that the parallel displacement is given by [see (3.1)]

$$r_{\|}=\frac{a}{(d-1)^{1/2}}\,(n_1+\cdots+n_{d-1}) \tag{3.18}$$

The kth-moment parallel correlation lengths are obtained as

$$[\xi_{\|}^{(k)}]^k=\left(\frac{a}{(d-1)^{1/2}}\right)^k\left[\left(z\frac{\partial}{\partial z}\right)^k G(z,\ldots,z;x_{\pm};w)\right]_{x_{\pm}=z}\Big/ Z(z;w) \tag{3.19}$$

Specifically, we calculated

$$\begin{aligned}\frac{(d-1)^{1/2}}{a}\,&\xi_{\|}^{(1)}(z;w)\\ &=(d-1)(1-z+2wz)^2\\ &\quad\times([(d+1)(1-z)+2dwz]\\ &\quad\times\{1-2z-(d-2)\,wz-[2(d-1)\,w^2-(d-2)w-1]\,z^2\})^{-1}\end{aligned} \tag{3.20}$$

and the appropriate scaling function [see (2.27)]

$$P_{\mathrm{PD}}^{(1)}(c\tau)=\frac{(d+1)(1+2\tau)^2}{[1+d(1+2\tau)][1-(d-2)\tau-2(d-1)\tau^2]} \tag{3.21}$$

The expressions for $\xi_{\|}^{(2)}(z;w)$ and also for $\xi_{\perp}^{(2)}(z;w)$ are extremely long and are not listed here. [The calculation of $\xi_{\perp}^{(2)}(z;w)$ can be accomplished by constructing the appropriate expression for $r_{\perp}^2$; compare (2.24)–(2.25). Details are omitted here.] We report the appropriate scaling functions [see (2.27)–(2.28)],

$$P_{\mathrm{PD}}^{(2)}(c\tau)=\left[\frac{d+1}{1+d(1+2\tau)}\right]^{1/2}\frac{1+2\tau}{1-(d-2)\tau-2(d-1)\tau^2} \tag{3.22}$$

$$[Q_{\mathrm{PD}}^{(2)}(c\tau)]^2=\frac{(d+1)[d+2(2d-1)\,\tau(1+\tau)+2\tau^3]}{d(1+\tau)[1+d(1+2\tau)][1-(d-2)\tau-2(d-1)\tau^2]} \tag{3.23}$$

4. DISCUSSION

It is obvious from the results reported in Sections 2 and 3 that the scaling functions remain nonuniversal for all finite $d \geqslant 2$. If Flory-type ideas of Nakanishi[5] have bearing for directed models, restoration of universality in the $d \to \infty$ limit may be anticipated.

The scaling-field combination

$$g = c\tau = cw\bar{N} \tag{4.1}$$

contains, in the $d \to \infty$ limit, additional unbounded parameter. Indeed, for both models considered,

$$c \approx d \qquad \text{as} \quad d \to \infty \tag{4.2}$$

see (2.17) and (3.15). As long as we define the scaling limit with fixed $dw\bar{N} = O(1)$, while d, w^{-1}, and $\bar{N}$ are large, we can formally expand the scaling functions in powers of $1/d$. Thus, we substitute $g/c(d)$ for τ and regard the scaling functions as functions of g and $1/d$. The result is extremely simple,

$$A(g, d), \quad B(g, d), \quad P^{(1,2)}(g, d), \quad [Q^{(2)}(g, d)]^2 \approx (1 - g)^{-1} \tag{4.3}$$

for both models. We also calculated the leading corrections to (4.3). (There are no corrections for the FD model A, B, and $P^{(1,2)}$.) It is interesting to note that the difference between the FD and PD scaling functions for the thermodynamic quantities, i.e., A and B, is of $O(d^{-3})$. The first-moment correlation length scaling functions $P^{(1)}$ differ in $O(d^{-2})$, while the second-order correlation length scaling functions $P^{(2)}$ and $Q^{(2)}$ are nonuniversal in $O(d^{-1})$.

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